

## **APPENDIX I**

### **Partition Coefficients For Thorium**

## Appendix I

### Partition Coefficients For Thorium

#### I.1.0 BACKGROUND

Two generalized, simplifying assumptions were established for the selection of thorium  $K_d$  values for the look-up table. These assumptions were based on the findings of the literature review conducted on the geochemical processes affecting thorium sorption. The assumptions are as follows:

- Thorium adsorption occurs at concentrations less than  $10^{-9}$  M. The extent of thorium adsorption can be estimated by soil pH.
- Thorium precipitates at concentrations greater than  $10^{-9}$  M. This concentration is based on the solubility of  $\text{Th}(\text{OH})_4$  at pH 5.5. Although (co)precipitation is usually quantified with the solubility construct, a very large  $K_d$  value will be used in the look-up table to approximate thorium behavior in systems with high thorium concentrations.

These assumptions appear to be reasonable for a wide range of environmental conditions. However, these simplifying assumptions are clearly compromised in systems containing high alkalinity (LaFlamme and Murray, 1987), carbonate (LaFlamme and Murray, 1987), or sulfate (Hunter *et al.*, 1988) concentrations, and low or high pH values (pH values less than 3 or greater than 8) (Hunter *et al.*, 1988; LaFlamme and Murray, 1987; Landa *et al.*, 1995). These assumptions will be discussed in more detail in the following sections.

Thorium  $K_d$  values and some important ancillary parameters that influence sorption were collected from the literature and tabulated. Data included in this table were from studies that reported  $K_d$  values (not percent adsorbed or Freundlich or Langmuir constants) and were conducted in systems consisting of:

- Low ionic strength ( $< 0.1$  M)
- pH values between 4 and 10.5
- Dissolved thorium concentrations less than  $10^{-9}$  M
- Low humic material concentrations ( $< 5$  mg/l)
- No organic chelates (such as EDTA)

These aqueous chemistry constraints were selected to limit the thorium  $K_d$  values evaluated to those that would be expected to exist in a far-field. The ancillary parameters included in these tables were clay content, calcite concentration, pH, and CEC. Attempts were also made to include the concentrations of organic matter and aluminum/iron oxides in the solid phase in the data set. However, these latter ancillary parameters were rarely included in the reports evaluated during the compilation of the data set. The data set included 17 thorium  $K_d$  values. The

descriptive statistics of the thorium  $K_d$  data set are presented in Table I.1. The lowest thorium  $K_d$  value was 100 ml/g for a measurement made on a pH 10 soil (Rancon, 1973). The largest thorium  $K_d$  value was 500,000 ml/g for a measurement made on a silt/quartz soil of schist origin (Rancon, 1973). The average thorium  $K_d$  value for the 17 observations was  $54,000 \pm 29,944$  ml/g.

**Table I.1.** Descriptive statistics of thorium  $K_d$  value data set presented in Section I.3.

	Thorium $K_d$ (ml/g)	Clay Content (wt.%)	pH	CEC (meq/100 g)	Calcite (wt.%)	Al/Fe- Oxides (wt.%)	Organic Matter (wt.%)
Mean	54,000	26.8	6.1	13.7	29	--	--
Standard Error	29,944	6.3	0.4	11.2	13.4	--	--
Median	5,000	30	6	2.9	25	--	--
Mode	100,000	40	6	2.9	0	--	--
Standard Deviation	123,465	14.1	1.5	29.8	30.1	--	--
Sample Variance	$1.5 \times 10^{10}$	199.2	2.1	886.2	905	--	--
Minimum	100	12	4	1.7	0	--	--
Maximum	500,000	40	10	81.2	60	--	--
No. Observations	17	5	17	7	5	0	0

## I.2.0 Approach and Regression Models

### I.2.1 Correlations with Thorium $K_d$ Values

A matrix of the correlation coefficients for thorium  $K_d$  values with soil parameters is presented in Table I.2. The correlation coefficients that are significant at or less than the 1 percent or 5 percent level of probability are identified. The parameter with the largest correlation coefficient with thorium  $K_d$  was pH ( $r = 0.58$ ,  $n = 16$ ,  $P \leq 0.01$ , where  $r$ ,  $n$ , and  $P$  represent correlation coefficient, number of observations, and level of probability, respectively). The pH range for this data set is 4 to 7.6. When  $K_d$  data for pH 10 is included in the regression analysis, the correlation coefficient decreases to 0.14 ( $n = 17$ ,  $P \leq 0.22$ ). The nonsignificant correlations with clay content, CEC, and calcite may in part be attributed to the small number of values in the data sets.

**Table I.2.** Correlation coefficients (r) of the thorium  $K_d$  value data set presented in Section I.3.

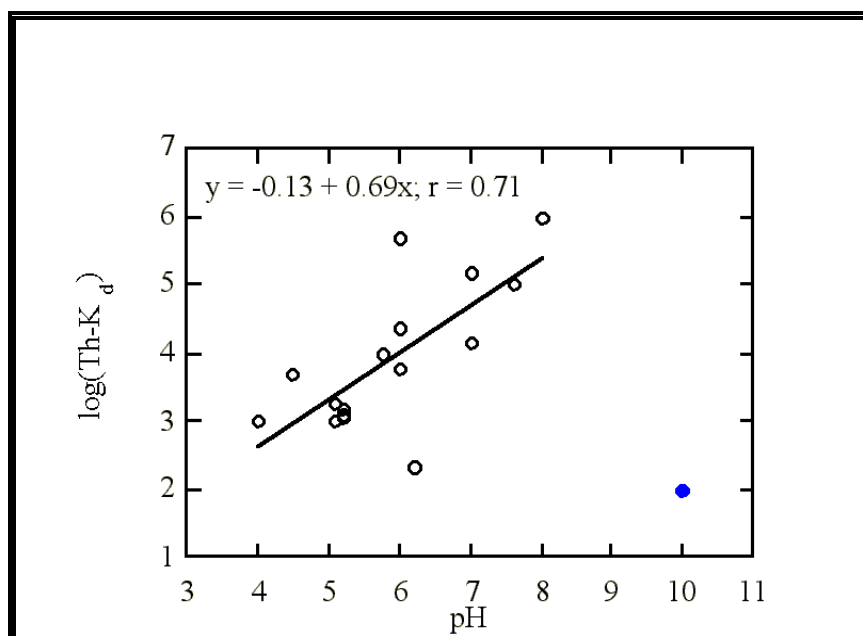
	Thorium $K_d$	Clay Content	pH	CEC
Thorium $K_d$	1			
Clay Content	-0.79	1		
pH	0.58 <sup>2</sup> (0.14) <sup>3</sup>	-0.84 <sup>1</sup>	1	
CEC	-0.15	--	-0.21	1
Calcite	0.76	-0.998 <sup>2</sup>	0.85 <sup>1</sup>	--

<sup>1,2</sup> Correlation coefficient is significant at the 5 percent ( $P \leq 0.05$ ) (indicated by footnote a) or 1 percent ( $P \leq 0.01$ ) (indicated by footnote b) level of significance, respectively. Significance level is in part dependent on the number of observations, n, (more specifically, the degrees of freedom) and variance of each correlation comparison (Table I.1). Thus, it is possible for thorium  $K_d$ /clay correlation coefficient of -0.79 to be not significant and the thorium  $K_d$ /pH correlation coefficient of 0.58 to be significant because the former has 4 degrees of freedom and the latter has 15 degrees of freedom.

<sup>3</sup> Excluding the  $K_d$  values at the highest pH value (pH 10), the correlation is 0.58 ( $n = 16$ ). Including this  $K_d$  value, the correlation coefficient decreases to 0.14.

### ***I.2.2 Thorium $K_d$ Values as a Function of pH***

Thorium  $K_d$  values were significantly correlated to pH between the pH range of 4 to 8, but were not correlated to pH between the range 4 to 10 (Figure I.1 and Table I.2). The pH dependence of thorium sorption to solid phases has been previously demonstrated with pure mineral phases (Hunter *et al.*, 1987; LaFlamme and Murray, 1987). The pH dependence can be explained in part by taking into consideration the aqueous speciation of thorium in groundwater. Thorium aqueous speciation changes greatly as a function of groundwater pH (Table I.3). As the pH increases, the thorium complexes become more anionic or neutral, thereby becoming less prone to be electrostatically attracted to a negatively charged solid phase. This decrease in electrostatic attraction would likely result in a decrease in  $K_d$  values. Figure I.1 shows an increase in thorium  $K_d$  values between pH 4 and 8. This may be the result of the pH increasing the number of exchange sites in the soil. At pH 10, the large number of neutral or anionic thorium complexes may have reduced the propensity of thorium to sorb to the soil.



**Figure I.1.** Linear regression between thorium  $K_d$  values and pH for the pH range from 4 to 8. [The single  $K_d$  value at pH 10 is identified by the filled circle.]

**Table I.3.** Calculated aqueous speciation of thorium as a function of pH. [The composition of the water and details of the aqueous speciation calculations are presented in Chapter 5. Total thorium concentration used in the aqueous speciation calculations is 1 ng/ml.]

pH	Dominant Aqueous Species	Percent (%) of Total Dissolved Thorium
3	$\text{ThF}_2^{2+}$ $\text{ThF}_3^+$	54 42
7	$\text{Th}(\text{HPO}_4)_3^{2-}$	98
9	$\text{Th}(\text{OH})_4^{\text{aq}}$	99

The regression equation between the pH range of 4 to 8 that is shown in Figure I.1 is

$$\log (\text{Th } K_d) = -0.13 + 0.69(\text{pH}). \quad (\text{I.1})$$

The statistics for this equation are presented in Table I.4. The fact that the P-value for the intercept coefficient is  $\geq 0.05$  indicates that the intercept is not significantly ( $P \geq 0.05$ ) different than 0. The fact that the P-value for the slope coefficient is  $\leq 0.05$  indicates that the slope is significantly ( $P \geq 0.05$ ) different than 1. The lower and upper 95 percent coefficients presented in Table I.4 reflect the 95 percent confidence limits of the coefficients. They were used to calculate the upper and lower limits of expected thorium  $K_d$  values at a given pH value.

### ***I.2.3 Approach***

Linear regression analyses were conducted with data collected from the literature. These analyses were used as guidance for selecting appropriate  $K_d$  values for the look-up table. The  $K_d$  values used in the look-up tables could not be based entirely on statistical consideration because the statistical analysis results were occasionally nonsensible. For example, the data showed a negative correlation between clay content and thorium  $K_d$  values. This trend contradicts well established principles of surface chemistry. Instead, the statistical analysis was used to provide guidance as to the approximate range of values to use and to identify meaningful trends between the thorium  $K_d$  values and the solid phase parameters. Thus, the  $K_d$  values included in the look-up table were in part selected based on professional judgment. Again, only low-ionic strength solutions similar to that expected in far-field ground waters were considered in these analyses.

**Table I.4.** Regression coefficient and their statistics relating thorium  $K_d$  values and pH.  
[ $\log (\text{Th } K_d) = -0.13 + 0.69(\text{pH})$ , based on data presented in Figure I.1.]

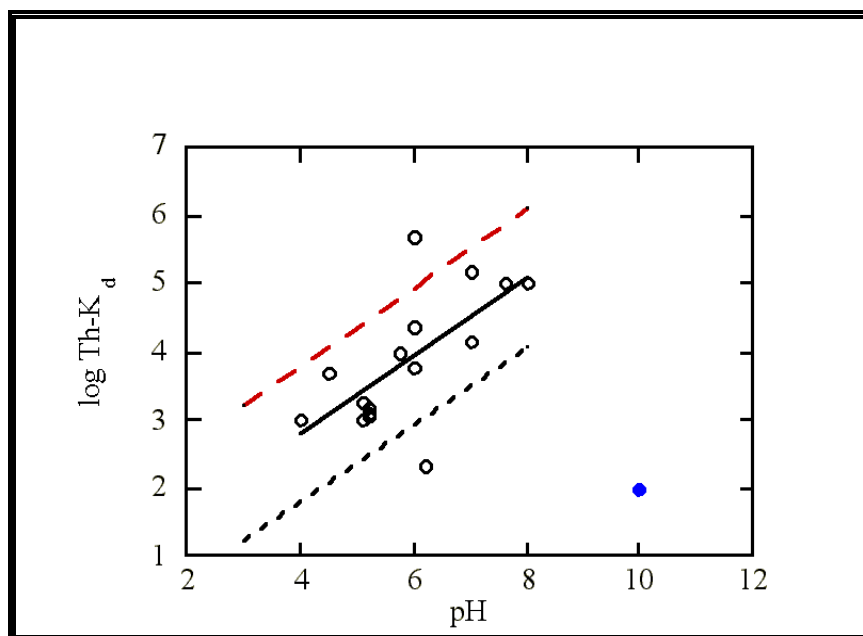
	<b>Coefficients</b>	<b>Standard Error</b>	<b>t-Statistic</b>	<b>P-value</b>	<b>Lower 95%</b>	<b>Upper 95%</b>
Intercept Coefficient	2.22	1.06	0.47	0.64	-1.77	2.76
Slope Coefficient	0.57	0.18	3.24	0.006	0.19	0.95

The look-up table (Table I.5) for thorium  $K_d$  values was based on thorium concentrations and pH. These 2 parameters have an interrelated effect on thorium  $K_d$  values. The maximum concentration of dissolved thorium may be controlled by the solubility of hydrous thorium oxides (Felmy *et al.*, 1991; Rai *et al.*, 1995; Ryan and Rai, 1987). The dissolution of hydrous thorium oxides may in turn vary with pH. Ryan and Rai (1987) reported that the solubility of hydrous thorium oxide is  $\sim 10^{-8.5}$  to  $\sim 10^{-9}$  in the pH range of 5 to 10. The concentration of dissolved thorium increases to  $\sim 10^{-2.6}$  M (600 mg/L) as pH decreases from 5 to 3.2. Thus, 2 categories, pH 3 - 5 and pH 5 - 10, based on thorium solubility were included in the look-up table. Although precipitation is typically quantified by the solubility construct, a very large  $K_d$  value was used in Table I.5 to describe high thorium concentrations.

The following steps were taken to assign values to each category in the look-up table. For  $K_d$  values in systems with pH values less than 8 and thorium concentrations less than the estimated solubility limits, Equation I.1 was used. This regression equation is for data collected between the pH range of 4 to 8 as shown in Figure I.1 [ $\log (\text{Th } K_d) = -0.13 + 0.69(\text{pH})$ ]. pH values of 4 and 6.5 were used to estimate the “pH 3 to 5” and “pH 5 to 8” categories, respectively. The  $K_d$  values in the “pH 8 to 10” category were based on the single laboratory experiment conducted at pH 10 that had a  $K_d$  of 200 ml/g. Upper and lower estimates of thorium  $K_d$  values were calculated by adding or subtracting 1 logarithmic unit to the “central estimates” calculated above for each pH category (Figure I.2). The 1 logarithm unit estimates for the upper and lower limits are based on visual examination of the data in Figure I.1. The use of the upper and lower regression coefficient values at the 95 percent confidence limits (Table I.5) resulted in calculated ranges that were unrealistically large. At pH 4, for the “pH 3 to 5” category, the lower and upper  $\log (\text{Th } K_d)$  values were calculated to be 1 and 6.6, respectively; at pH 6.5, this range of  $K_d$  was -0.5 to 9.0). All thorium  $K_d$  values for systems containing concentrations of dissolved thorium greater than their estimated solubility limit ( $10^{-9}$  M for pH 5 to 10 and  $10^{-2.6}$  M for pH < 5) were assigned a  $K_d$  of 300,000 ml/g.

**Table I.5.** Look-up table for thorium  $K_d$  values (ml/g) based on pH and dissolved thorium concentrations. [Tabulated values pertain to systems consisting of low ionic strength (<0.1 M), low humic material concentrations (<5 mg/l), no organic chelates (such as EDTA), and oxidizing conditions.]

$K_d$ (ml/g)	pH					
	3 - 5		5 - 8		8 - 10	
	Dissolved Th (M)		Dissolved Th (M)		Dissolved Th (M)	
	< $10^{-2.6}$	> $10^{-2.6}$	< $10^{-9}$	> $10^{-9}$	< $10^{-9}$	> $10^{-9}$
Minimum	62	300,000	1,700	300,000	20	300,000
Maximum	6,200	300,000	170,000	300,000	2,000	300,000



**Figure I.2.** Linear regression between thorium  $K_d$  values and pH for the pH Range 4 to 8. [Values  $\pm 1$  logarithmic unit from the regression line are also identified. The single  $K_d$  value at pH 10 is identified by the filled circle)].

### I.3.0 $K_d$ Data Set for Soils

The data set of thorium  $K_d$  values used to develop the look-up table are listed in Table I.6.



**Table I.6.** Data set containing thorium  $K_d$  values.

Thorium $K_d$ (ml/g)	pH	Clay (wt.%)	CEC <sup>1</sup> (meq/ 100g)	OM <sup>1</sup> (wt.%)	Fe- Oxides (wt.%)	Th (M)	Calcite (wt.%)	Solution Chemistry	Soil ID and Characteristics	Ref <sup>2</sup>
10,000	7.6		3					Synthetic GW <sup>1</sup> , pH 6.6	Soil A	1
500,000	6	40					0	Syn. GW, <sup>232</sup> Th Competing Ion	Silt+Qtz Sed., Schist soil	2
1,000	4	40					0	Syn. GW, <sup>232</sup> Th Competing Ion	Silt+Qtz Sed., Schist soil	2
100,000	8	12					60	Syn. GW, <sup>232</sup> Th Competing Ion	Silt+Qtz+OM+calcite, Schist Soil	2
150,000	7	30					25	Syn. GW, <sup>232</sup> Th Competing Ion	Cadarache Sed.	2
100	10	12					60	Syn. GW, <sup>232</sup> Th Competing Ion	Silt+Qtz+OM+calcite, Schist Soil	2
24,000	6							Groundwater	Glacial till, Clay	3
5,800	6							Groundwater	Fine Coarse Sand	3
1,028.6	5.1		2.9						Gleyed Dystric Brunisol, Ae Horizon 4-15 cm	4
1,271	5.2		2.1						Gleyed Dystric Brunisol, Bf Horizon 1 5-45 cm	4
5,000	4.5								Jefferson City, Wyoming, Fine Sandstone and Silty Clay	5
10,000	5.8								Jefferson City, Wyoming, Fine Sandstone and Silty Clay	5
15,000	7								Jefferson City, Wyoming, Fine Sandstone and Silty Clay	5
1,578	5.2		81.2					Groundwater	Gleyed Dystric Brunisol, Ah Horizon	6
1,862.5	5.1		2.9					Groundwater	Gleyed Dystric Brunisol, Ae Horizon	6
1,153.7	5.2		2.1					Groundwater	Gleyed Dystric Brunisol, Bf Horizon	6
206.9	6.2		1.7					Groundwater	Gleyed Dystric Brunisol, C Horizon	6

<sup>1</sup> CEC = cation exchange capacity, OC = organic matter, GW = groundwater.

<sup>2</sup> References: 1 = Legoux *et al.*, 1992; 2 = Rancon, 1973; 3 = Bell and Bates, 1988; 4 = Sheppard *et al.*, 1987; 5 = Haji-Djafari *et al.*, 1981; 6 = Thibault *et al.*, 1990.

## I.5.0 References

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